SPECTROSCOPIC CONSTANTS OF MOLECULES VII. RELATION BETWEEN FORCE CONSTANT AND EQUILIBRIUM INTERNUCLEAR DISTANCE FOR HYDRIDE DIATOMS

YATENDRA PAL VARSHNI, SHASHANKA SHEKHAR MITRA* AND RAMESH CHANDRA SHUKLA

DEPARTMENT OF PHYSICS, ALLAHABAD UNIVERSITY, ALLAHABAD

(*Received, May* 15, 1959)

ABSTRACT For hydride diatoms a relation between the force constant k_e and equilibrium internuclear distance r_e has been suggested: $k_e r_e^4 = C$, where C is a constant depending on the type of the linkage. The validity of the relation for ground and excited states of various hydride diatoms has been examined

INTRODUCTION

It is well known that in a particular molecule the force constant and the internuclear distance vary in an inverse fashion, and numerous relations have been suggested connecting the two Recently Varshni (1958) has given a brief survey of the different relations (see also Baughan, 1957) In the present paper we will investigate a formula connecting k_e and r_e for all states (ground as well as excited) of the various hydride diatoms.

Hydride diatoms differ somewhat from other diatoms in the fact that they show regular variation in properties, not only in a molecular group, but also in is molecular period (Clark 1936, Clark and Stoves 1936, Berriman and Clark 1938, Clark 1950a,b, Sheline 1950) The same is true for deuterides (Clark 1949,

TABLE I

Nomenclature	Diatoms covered
$s\sigma$	HH, 1a–H, 1b–H
$d\sigma$	CaH, SrH, BaH
$p\sigma$	BeH, MgH, ZnH, CdH HgH, 3b–H
$p\pi$	4b–H, 5b–H, 6b–H, 7b–H
$7a$–H	MnH, etc.
8–H	CoH, NiH, etc.

* Now at Division of Pure Chemistry, National Research Council, Ottawa, Canada.

1950b). Clark (1936) has classified hydride diatoms and diatom ions according to the type of linkage. As we will make use of his classification, we summarize it in Tables I (neutral hydrides) and II (ionized hydrides).

TABLE II

Nomenclature	Diatoms covered
$s\sigma$	BeH^+, MgH^+, ZnH^+, CdH^+, HgH^+
$p\sigma$	$3b\text{–}H^+$, $4b\text{–}H^+$
$p\pi$	$5b\text{–}H^+$, $6b\text{–}H^+$, $7b\text{–}H^+$

Clark's classification of MnH is uncertain, and he has not classified CoH and NiH. We have put the last two together.

The various relations which have been proposed between k_e and r_e have been given by Herzberg (1950) and Varshni (1955,1958) Here we quote only a few of them, which have been applied on sufficient number of hydrides.

Badger (1934) :

$$k_e(r_e - d_{ij})^3 = \text{const} \quad \ldots (1)$$

where d_{ij} is a constant depending on molecular period.

Clark (1935) .

$$\omega_e r_e^3 n^{\frac{1}{2}} = k - k' \quad \ldots (2)$$

where n is the group number, equal to the total number of valency electrons of the atoms concerned (e.g. 2 for H_2, 5 for CH etc.), and $(k - k')$ is a constant.

Allen and Longair (1935) :

$$k_e r_e^6 = \text{const.} \quad \ldots (3)$$

where the constant is assumed to be the same for all molecules of a molecular period.

Huggins (1935, 1936) .

$$r_e = r_{12} - (2.303 \log C)/a \quad \ldots (4)$$

where

$$C = 5.85 \times 10^{-6} \mu \omega_e^2/(a^2 - aa')$$

$$a' = (2.0625a^2 + 0.7154\mu\omega_e x_e)^{\frac{1}{2}} - 1.75a$$

Clark and Stoves (1939) have compared the above four equations. Their calculations of r_e by various formulae on about 50 states of hydride diatoms and diatom ions showed that Clark's formula gives the best results.

NEW FORMULA

Birge (1925) and Mecke (1925) have observed that for the different electronic states of one and the same molecule, the following relation holds :

$$\omega_e r_e^2 = \text{const.} \quad \ldots (5)$$

It has been found that a modification of this relation can be successfully used for hydride diatoms and diatom ions for ground as well as excited states.

The modified relation is

$$k_e r_e^4 = C = \text{constant} \qquad (6)$$

The constant depends on the type of binding and the molecular period to which that diatom in question belongs

The values of C, for neutral diatoms (when k_e is in 10^5 dynes/cm. and r_e in Angstroms), for different types of binding as classified by Clark (1936), have been given in Table III.

TABLE III

Period	Type of binding					
	$s\sigma$	$p\sigma$	$p\pi$	$d\sigma$	7σ–H	$8\ H$
HH	2 03					
KH	6 634	7 2	6.8			
LH	9 91	11 4	13 5			
MH	14.56			15 1	11.63	11 035
$\bar{M}H$	9 9	10 4	16 45			
NH	16.16			18 7		
NH	12 1	12 7	20 79			
OH	18 08			20 4		
OH	14 9	13 4	17.1			

Values of the constant C for ionized hydrides have been tabulated in Table IV

TABLE IV

Period	Type of binding		
	$s\sigma$	$p\sigma$	$p\pi$
HH^+	1.973		
KH^+	7 80	6.75	5.466
LH^+	11 95	10.52	10 08
MH^+	10.3		
$\bar{N}H^+$	12 7		
$\bar{O}H^+$	14.2		

Clark's equation was tested by Clark and Stoves (1939) by using the molecular constants then available. Some of these values have changed, in some

cases appreciably, with improved determinations in recent years. Hence to see the relative merits of our equation and that of Clark, it was necessary to redetermine the constant in Clark's equation. The new values of $(k-k')$ are shown in Tables V and VI.

The constants 'C' and $(k-k')$ were determined as follows

Equation (6)—In most of the cases, constant C was determined by taking the mean value of $k_e r_e^4$ of the states of a particular type of binding (in some cases the 4th significant figure has been rounded up). But states showing abnormal value of $k_e r_e^4$ were left out. viz.. one state in each of LiH, NaH, KH, RbH, CsH, CaH, SrH, and CH^+.

Clark's equation (2)—The constant $(k-k')$ was also determined by taking the mean of $\omega_e r_e^3 n^{\frac{1}{2}}$ of the states of a particular type of binding, except the following cases—ground state of H_2, 1 excited state in each of alkali hydrides, CaH and SrH. This point is discussed more fully later on

Numerical results by the two equations have been reported in Tables VII and VIII where only one state was available for determining the constant, 'calculated r_e' has been omitted. Uncertain values are enclosed in parentheses. Percentage errors in brackets have not been taken into account for calculating average percentage errors.

RESULTS

All data have been taken from Herzberg (1950). Data in square brackets refer to the lowest vibrational level, or the two lowest, or three lowest. Usually we have not considered such states, tabulated by Herzberg, for which the constants appear to be too much uncertain.

TABLE V

Constant $(k-k')$ for neutral hydride diatoms

(ω_e in cm^{-1} and r_e in A.)

Period	Type of binding					
	$s\sigma$	$p\sigma$	$p\pi$	$d\sigma$	$7a$–H	8–H
HH	3899					
KH	8066	8636	8952			
LH	11139	13756	17005			
MH	15740			17419	21867	19689
MH	8849	11346	21188			
NH	17569			20426		
NH	10460	15683	26957			
OH	19540			22757		
$\overline{OH}$	11297	15994	23768			

TABLE VI

Constant $(k-k')$ for hydride diatom ions

Period	Type of binding		
	$s\sigma$	$p\sigma$	$p\pi$
HH$^+$	2736		
KH$^+$	7896	7529	7886
LiH$^+$	11840	11847	15420
MH$^+$	9579		
NH$^+$	11557		
OH$^+$	11377		

TABLE VII

Hydride Diatoms

Period	Diatom and type	State	ω_e	k_e	r_e obs.	Eq (6) This paper r_e calc.	Eq (6) This paper % Error	Clark eqn. r_e calc	Clark eqn. % Error
HH	H_2	a	(2339)	(1.625)	(1 072)	1 057	−1 41	1 056	−1.49
	$s\sigma$	a'	2322	1.601	1 057	1 061	+0 38	1 059	+0 19
		k	2336	1 620	1 067	1.058	−0.84	1 057	−0 94
		h	2395.2	1.702	1.045	1.045	0	1 048	+0 29
		d	2371.6	1.669	1.050	1.051	+0.09	1 052	+0.19
		e	2195.8	1.431	1 107	1.091	−1.44	1 079	−2.53
		a	2664 8	2.107	0 9887	0 9908	+0 21	1.012	+2.36
		c	2465.0	1.803	1 038	1.030	−0.77	1.038	0
		D	2325 1	1.604	1 034	1.060	+2.51	1.059	+2 42
		J	[2220]	[1.463]	(1.077)	1.085	+0 74	1.075	−0.19
		I	2265.2	1.523	1.060	1.074	+1 32	1.068	+0.75
		H	2588 9	1.989	1.012	1 005	−0 69	1 021	+0 89
		G	2442.7	1.771	1 033	1.035	+0.19	1.041	+0 77
		B	1356.9	0 5467	1 293	1 388	+7 35	1 267	−2.01
		A	1395.2	5 735	0 7417	0 7713	+3.99	0 856	(+15.41)
KH	LiH	A	*231 11	0 02851	2.596	3.906	(+50 46)	2 898	(+11 63)
	$s\sigma$	X	1105 65	1 025	1 595				
	BeH	B	[2133 1]	[2.430]	[1 321]	1.312	−0 08	1.327	+0.45
	$p\sigma$	A	2087 7	2 317	1.333	1.327	−0 45	1.337	+0.30
		X	2058 6	2 262	1 343	1.336	0 52	1 343	0
	BH	B	(2400)	(3 132)	1 215	1 231	+1 32	1.216	+0 08
	$p\sigma$	A	(2344)	(2 987)	1 226	1 246	+1.63	1.226	0
		X	(2366)	(3 045)	1 232	1 240	+0 65	1 222	0.81
	CH	C	2824.1	4 366	1.113	1.117	−0 36	1.123	+0.90
	$p\pi$								
		B	2542.5	3 539	1 186	1 178	−0 67	1.163	1.94
		A	2921 0	4 672	1 103	1 098	−0 45	1 124	+1 90
		X	2861 6	4 485	1 120	1.110	−0 89	1.119	0 09
	NH	C	2612	3.777	[1 125]	1 158	+2.93	1.119	−0 53
	$p\pi$	A	(3300)	(6 030)	1.037	1.030	−0 67	1 035	−0 19
		a	[3186]	[5 619]	[1 044]	1 049	+0.48	1.047	+0.29
		X	(3300)	(6.030)	1.038	1.030	−0.77	1.035	−0.29
	OH	A	3180 6	5.648	1.0121	1.047	+3 46	1 021	+0 88
	$p\pi$	X	3735.2	7 791	0 9706	0.9665	−0 42	0 9676	−0.31
	HF	X	4138.5	9 654	0.9171	0.9171	−0 11	0.9145	−0.28
	$p\pi$								

(TABLE VII (contd.)

Period	Diatom and type	State	ω_e	k_e	r_e obs.	Eq. (6) This paper		Clark eqn.	
						r_e calc	% Error	r_e calc.	% Error
LH	NaH	A	310.6	0 05487	3.208	3.664	(+14.22)	2.938	(−8.42)
	$s\sigma$	X	1172.2	0.7816	1.887				
	MgH	D	(1620)	(1 495)	[1.664]	1.662	−0.12	1 699	+2.10
	$p\sigma$	C	1740	1 724	1.682	1 003	−4 70	1 659	−1.37
		A	1611.3	1 479	1.679	1 666	−0.77	1.702	+1.37
		X	1495 7	1.275	1.731	1 729	−0 12	1 744	+0.75
	AlH	C	1575 3	1.420	1 613	1.683	+4 34	1.634	+1.30
	$p\sigma$	b	(1683)	(1 631)	[1 602]	1.626	+1 50	1.599	−0 19
		a	(1688)	(1 631)	[1.609]	1.626	+1.06	1.597	−0.75
		X	1682 6	1 620	1 646	1 628	−1 09	1 599	−2.86
	SiH	X	(2080)	(2.479)	1.520	1 528	+0.53	1 541	+1 38
	$p\pi$								
	PH	X	(2380)	(3 257)	[1.433]	1.427	-0 24	1.429	−0.28
	$p\pi$								
	ClH	X	2989 7	5 157	1.275	1 272	0 24	1.262	−1.02
	$p\pi$								
MH	KH	A	251 0	0.03646	3 61	4 470	(+23 82)	3.539	(- 1.97)
	$s\sigma$	X	985.0	0 5744	2.244				
	CaH	C	1444	1 208	[1 892]	1 880	- 0.63	1 910	+0 95
	$d\sigma$	D	1149	0.7647	2.62	2 109	(−19 46)	2 061	(−21 3)
		E	1248.6	0 9026	[2.000]	2.023	+1.15	2 004	+0.2
		B	1285	0 9561	1 954	1 993	+2.00	1 985	+1 59
		A	1333	1 029	1.99	1.957	1.66	1.961	+1 46
		X	1299	0.9774	2.002	1 983	−0.95	1.978	-1 20
	MnH	X	[1490.6]	[1.295]	1.731				
	$7a$-H								
	CoH	X	(1890)	(2.085)	[1.543]	1 517	- 1.69	1 514	−1 88
	8-H								
	NiH	X	[1926.6]	[2 166]	1.475	1.502	+1 83	1.505	+2 03
	8-H								
MH	CuH	D	[1803 9]	[1.901]	1.482	1.510	+1.89	1 514	+2 16
	$s\sigma$	B	[1562.3]	[1.308]	1.607	1 659	+3 21	1.588	−1 18
		A	1698 4	1 686	1 572	1 557	−0.95	1 545	-1.72
		X	1940.4	2 200	1.463	1 456	-0 48	1 477	+0 96
	ZnH	A	1910.2	2 132	1 511	1.486	-1.65	1 508	−0.20
	$p\sigma$	X	1607 6	1.510	1.594	1 620	+1 63	1 597	+0 19
	BrH	X	2649.7	4 115	1 414				
	$p\pi$								
NH	RbH	A	244.6	0 03512	3.708	4.631	(+24.89)	3.703	(−0.14)
	$s\sigma$								
		X	936 77	0 5148	2.367				
	SrH	C	1347	1.065	2.054	2.046	-0.39	2 061	+0.34
	$d\sigma$	D	1014.1	0.6034	2 964	2.359	(−20.42)	2.266	(−23.55)
		X	1206 2	0 8535	2 1455	2.163	+0.84	2 138	−0 35
NH	AgH	A	1663 6	1.628	1.641	1.651	+0.61	1.644	+0.18
	$s\sigma$	X	1760 0	1.822	1.617	1.605	−0.74	1 614	−0.19
	CdH	A	1758 1	1.819	1.663	1.626	- 2.22	1.727	+3.85
	$p\sigma$	X	1430 7	1.204	1.762	1.802	+2.27	1.850	+4.99
	InH	B	1491	1 308	1.761	1 765	+0.23	1.739	−1.25
	$p\sigma$	A	1458 4	1 252	1.773	1.784	+0.62	1.752	−1.18
		X	1474 7	1.280	1.838	1.774	−3 48	1 745	−5.06
	IH	X	2309 5	3.141	1.604				
	$p\pi$								

TABLE VII (contd.)

Period	Diatom and type	State	ω_e	k_e	r_e obs.	Eq. (6) This paper r_e calc.	Eq. (6) This paper % Error	Clark eqn. r_e calc.	Clark eqn. % Error
OH	CsH	A	204.0	0.02451	3 869	5.212	(+34 71)	4.076	(+5.35)
	$s\sigma$	X	890 7	0 4673	2.494				
	BaH	C	1323	1 031	2 18	2.109	−3 21	2 149	−1.42
	$d\sigma$	E	1231	9 8928	2 198	2 186	−0.55	2.202	+0.18
		B	1088	0 6977	2 271	2 326	+2 42	2.294	+1.01
		X	1172	0 8097	2 232	2 241	+0 40	2.238	+0.27
ŌH	AuH	A	1669.5	1.646	1.673	1.735	+3.71	1.685	+0.72
	$s\sigma$	X	2305.0	3.136	1 524	1.477	3 08	1.513	−0.72
	HgH	A	2065.8	2.522	1.586	1.518	−4.29	1.647	+3.85
	$p\sigma$	X	1387.09	1 137	1 740	1.853	+6.50	1.881	+8.10
	TlH	C	[1269.5]	[0.9519]	1.944	1 936	−0.41	1.847	−4.99
	$p\sigma$	X	1390 7	1 142	1.877	1 851	−1.39	1.792	−4.53
	PbH	X	1564.1	1 444	1 839	1.855	+0 87	1.894	+2.99
	$p\pi$								
	BiH	C	[1313.6]	[1.019]	1.96	2.024	+3 06	1 947	−0.66
	$p\pi$	B	(1728)	(1 763)	1 780	1.765	0 84	1 777	−0 17
		A	1739.4	1.786	1.788	1 759	−1.62	1 774	−0.78
		X	1698.9	1.706	1.809	1 779	−1 66	1.788	−1 16
						Average	+1.48		1.20

TABLE VIII

Hydride diatom—ions

Period	Diatom and type	State	ω_e	k_e	r_e obs	Eq. (6) r_e calc.	Eq. (6) % Error	Clark eqn. r_e calc.	Clark eqn. % Error
HH⁺	HH⁺	X	2297	1 563	1 060				
	$s\sigma$								
KH⁺	BeH⁺	A	1476 1	1 163	1 609	1 609	0	1.558	−3.17
	$s\sigma$	X	2221 7	2.636	1.312	1 311	−0 08	1.360	+3.66
	BH⁺	A	(2235)	(2 717)	1.256	1.255	−0.08	1 248	−0.64
	$p\sigma$	X	(2435)	(3.225)	1.215	1.203	−0.99	1 213	−0.16
	CH⁺	A	1850.0	1.875	1.234	1.377	(+11.59)	1 267	+2.67
	$p\sigma$	X	[2739 5]	[4.111]	1.131	1 131	0	1.112	−1 68
	OH⁺	X	[2955]	4.875	1 029				
	$p\pi$								
LH⁺	MgH⁺	A	1132.7	0 731	2.006	2.011	+0.25	1.948	−2.89
	$s\sigma$	X	1695.3	1.638	1.649	1.643	−0 36	1.703	+3.27
	AlH⁺	A	(1753)	(1.758)	1 591	1.564	−1.70	1 574	−1.07
	$p\sigma$	X	(1610)	(1 483)	1 602	1.632	+1.87	1.620	+1.12
	ClH⁺	A	1605 8	1.488	1 514	1.613	+6 54	1 537	+1.52
	$p\pi$	X	2675 4	4.130	1.315	1 250	−4 94	1.296	−1.44
M̄H⁺	ZnH⁺	A	1365	1.089	1.716	1.754	+2.21	1.706	−0.58
	$s\sigma$	X	1916	2 146	1.514	1 480	−2.25	1 523	+0.59
N̄H⁺	CdH⁺	A	1252	0.9223	1.865	1.927	+3.32	1.869	+0.21
	$s\sigma$	X	1775	1.855	1.667	1 617	−3.00	1 664	−0.18
ŌH⁺	HgH⁺	A	1621.0	1 552	1 692	1.739	+2.78	1.706	+0.83
	$s\sigma$	X	2033.9	2.442	1.594	1.552	−2.63	1.581	−0.82
						Average	+1.94		1.47

DISCUSSION

Equation 6 —When the values are calculated according to equation 6, it will be observed that, except the eight cases where the percentage errors are large (>10%) (errors shown in parentheses), the agreement between the calculated and the observed values is quite satisfactory The mean percentage error for 80 states of neutral diatoms is 1 48 and that for 17 states of ionized diatoms 1.94.

But when they are calculated according to Clark equation (2) the results are slightly better than our equation The mean percentage error for 79 states of neutral diatoms is 1.29 and that for 18 states of ionized diatoms 1.47 . Errors enclosed in brackets have not been taken into account for calculating the mean percentage errors.

TABLE IX

Formula	No of neutral diatom states	Average % error	No of diatom ion states	Average % error	Total no of states	Average % error
Equation 6 (Present work)	80	1 48	17	1.94	97	1.56
Clark eqn. 2	79	1 29	18	1.47	97	1.33
From Clark and Stoves' paper.						
Allen-Longair	41	4 41	11	6 24	52	4 79
Badger	41	3 37	11	4 53	52	3.61
Huggins	41	2 60	11	2 36	52	2 55
Clark	39	1 17	10	1 48	49	1 23

The percentage errors by the two equations are summarized in Table IX. To give some idea of the results by other equations, average percentage errors for the different equations as calculated from the results given in Clark and Stoves (1939) paper are also given in Table IX Their results on deuterides and excited states of alkali hydrides were left out. It may be emphasised that these results refer to the molecular constants then available.

Force constants of corresponding states of isotopic molecules are same and the internuclear distances are also almost the same (r_e for hydrides and corresponding deuterides rarely differ by more than 0.001A) Hence formula (6) will be equally applicable to isotopic molecules like deuterides.

The cases for which large percentage errors have been found are interesting.

Alkali hydrides—For the sake of uniformity the values of constants in both equations were found from the ground state only. The percentage errors for the excited states are shown in Table X.

TABLE X

Diatom	State	% error Eq. (6)	% error Clark eqn.
LiH	A	+ 50 46	+ 11 63
NaH	A	+ 14 22	− 8.42
KH	A	+ 23.82	− 1.97
RbH	A	+ 24 89	− 0.14
CsH	A	+ 34.71	+ 5 35
CaH	D	−19.46	−21.34
SrH	D	−20 42	−23.55

It is knownth at all the five excited states of alkali hydrides are abnormal in that their $\omega_e x_e$ is negative. The coincidence that equation (6) gives uniformly high positive errors for them is of some significance

CaH and SrH—Both C and D states of these are known to show strong perturbations. Both the equations give high negative errors for state D (Table X) of each. Corresponding state of BaH has not been observed. It may be that when this state is observed, it may also show perturbations.

One state of CH^+ gives large error by eq. (6) and so is the case for the ground state of H_2 by Clark equation.

Finally, from these and the previous results it may be concluded that Clark equation still retains its best merit with equation (6) giving a much closer approach to it than others

ACKNOWLEDGMENTS

One of the authors (Y.P.V.) is thankful to the U.P. Scientific Research Committee for a research grant. Thanks are also due to Mr. S. N. Srivastava for checking some of the results.

REFERENCES

Allen, H. S and Longair, A. K., 1935, *Phil. Mag.*, **19**, 1032
Badger, R. M., 1934, *J. Chem. Phys*, **2**, 128.
Baughan, E. C., 1957, *Trans. Faraday Soc.*, **53**, 1046.
Borriman, R. W. and Clark, C. H. D., 1938 *Proc. Leeds Phil. Soc.*, **3**, (8), 465,

Birge, R. T., 1925, *Phys. Rev.*, **25**, 240 (Formula quoted by Morse, P. M., 1929, *Phys. Rev.*, **34**, 57)

Clark, C. H. D., 1935, *Phil. Mag*, **19**, 476.

Clark, C. H. D., 1936, *Proc. Leeds. Phil. Soc.*, **3**, (4), 218.

Clark, C. H. D., 1949, *Proc. Leeds Phil. Soc.*, **5** 244.

Clark, C. H. D., 1950*a*, *Nature*, **165**, 1011.

Clark, C. H. D., 1950*b*, *Proc. Leeds Phil. Soc.*, **5**, 318.

Clark, C. H. D. and Stoves, J. L., 1936, *Proc. Leeds Phil. Soc.*, **3**, (4), 221.

Clark, C. H. D. and Stoves, J. L., 1939, *Phil. Mag.*, **27**, 389.

Herzberg, G., 1950, Spectra of Diatomic Molecules (D Van Nostrand Co., Inc., New York).

Huggins, M. L., 1935, *J. Chem. Phys.*, **3**, 473.

Huggins, M. L., 1936, *J. Chem. Phys.*, **4**, 308.

Mecke, R., 1925, *Z. Phys.*, **32**, 823.

Shelme, R. K., 1950, *J. Chem Phys.*, **18**, 927.

Varshni, Y. P., 1955, Thesis, Allahabad University.

Varshni, Y. P., 1958, *J. Chem Phys*, **28**, 1081.